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CATALYTIC REDUCTION OF OXIDES OF NITROGEN

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CATALYTIC REDUCTION OF OXIDES OF NITROGEN

FINAL REPORT

ON

USPH GRANT AP-00387

FOR THE PROJECT PERIOD

DECEMBER 1, 1967 - NOVEMBER 30, 1970

PRINCIPAL INVESTIGATORS: PROF. EUGENE E. PETERSEN
PROF. ALEXIS T. BELL

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This report describes work which has been completed and that which was in progress for the project period extending from December 1, 1967, to November 30, 1970. During this period five students received the masters degree while working on the project and one new student began work on a doctoral thesis.

Most of the work during the current project period was devoted to the completion of investigations of the steady state kinetics for the reduction of nitric oxides by carbon monoxide, hydrogen, and a series of hydrocarbons. In addition two new projects were initiated. The first of these was directed at studying the effects of the state of oxidation of a copper chromite catalyst on its activity for the CO-NO reaction. The second project involved an investigation of the adsorbed species present on the catalyst surface. The purpose of this work was to determine the mechanism by which N_2 and N_2O are formed during the reduction of NO.

Work on the catalytic reduction of nitric oxide with ethane was successfully completed by Mr. R. K. Mahendroo. These studies were carried out in a differential flow reactor filled with a barium-promoted copper chromite catalyst (Girdler G-22). Ethane and nitric oxide concentrations were varied from 50 to 500 ppm with helium as diluent. The only significant reaction products were nitrogen, carbon dioxide and water. Data were obtained at atmospheric pressure and at temperatures of 360, 390, and 420°C. An attempt to fit simple Hougen-Watson models yielded unrealistically large values for some of the parameters. These models were therefore considered to be inadequate for representing the phenomena actually occurring on the catalyst surface under the conditions studied. An empirical rate expression,

$$r = 1.02\left[\exp(-9{,}200/RT)\right] P_{C_2H_6}^{0.6} P_{NO}^{0.4},$$

was found to fit the data well over the range of conditions which had been considered.

Further work on the reduction of nitric oxide by hydrocarbons was undertaken by Mr. J. Ault. In this work methane, ethane, ethylene, propane, propylene, acetylene, n-hexane, benzene, and n-octane were examined as possible reducing agents. A barium-promoted copper chromite catalyst was used in a flow reactor operated at atmospheric pressure and temperatures of 225 to 525°C. Nitric oxide inlet concentrations were held at 10,000 ppm while hydrocarbon inlet concentrations were set at 10 percent excess over that required for complete nitric oxide reduction. The only reaction products observed were carbon dioxide, nitrogen, and water.

In general, an increase in carbon number in the hydrocarbons studied resulted in a decrease in the required temperature for a given nitric oxide conversion. For a given carbon number the required temperature for a given nitric oxide conversion decreased

with the degree of saturation. Using an integral analysis, the data were correlated by empirical rate expressions based on an irreversible reaction apparently one-half order in nitric oxide and one-half order in hydrocarbon.

For each NO-hydrocarbon reaction investigated, catalyst deactivation rates were determined in runs usually lasting 150 hours or more. Typically the rates were approximately 5 percent decrease per 100 hours of operation, in a "standard" run. The NO-acetylene reaction produced the highest decline in catalyst activity, 18.3 percent decrease per 100 hours.

A study of the reduction of nitrogen dioxide with hydrogen has also been completed. This work was carried out by Mr. A. Amirnazmi. In the initial states of the investigation the activities of four commercial catalysts were explored. The effectiveness of these catalysts is given in Table I.

Table I.

Comparison of Effectiveness of Various Catalysts

Weight of Catalyst = 5.0 g
Total flow = 2800 cc/min (92.5% He, 4% H_2, 3.5% NO_2)

Catalyst	Temp. (°C)	% H_2 Conversion
Copper-zinc-chrome (Girdler G-50)	250	10
Barium-promoted copper chromite (Girdler G-22)	240	21
Platinum on alumina (Girdler G-43)	260	83
Chromium-promoted iron oxide (Girdler G-3A)	252	7

The platinum catalyst, G-43, was found to be most active but led to large temperature gradients in the reactor and difficulties in temperature control. For this reason the barium-promoted copper chromite catalyst was selected for further investigation. Differential kinetic data were taken on a flow reactor operating at atmospheric pressure and at temperatures of 160 to 270°C. Reactant partial pressures were varied from 0.007 to 0.1 atm. Nitrogen, ammonia, and water were the only products formed, and it was observed that the relative abundance of nitrogen increased with space velocity. It was found that the kinetic data could be fitted by a rate expression of the form:

$$r = \frac{k\, P_{H_2}^{1.3}}{1 + K_{NO_2} P_{NO_2}}$$

where $k = 7.1\times10^{3} \exp(-15/RT)$ (gmoles)/(min)(g cat.)(atm.)$^{1.3}$ and $K_{NO_2} = 6.9\times10^{-7} \exp(20/RT)$ atm^{-1}.

An extension of the earlier work of Ayen and Ng [Air Water Pollut. Int. J. 10, 1 (1966)] has been completed recently by Mr. E. Force. Differential kinetic data were obtained in a recycle reactor system over the temperature range of 240-500°C and NO concentrations of 50-5000 ppm. These data were fitted to various Langmuir-Hinshelwood-Hougen-Watson rate equations using a nonlinear least-squares digital computer program. The rate equation below gave the best fit to all the data (± 7.2% relative deviation) when the constants were required to obey an exponential temperature dependence.

$$(-r_{NO}) = \frac{k_s K_{NO} K_{CO} P_{NO} P_{CO}}{(1 + K_{NO} P_{NO} + K_{CO} P_{CO})^2}$$

where $k_s = 15.7 \exp(-10{,}160/RT)$, gmole/(g min)

$K_{NO} = 0.034 \exp(7{,}560/RT)$, atm^{-1}, and

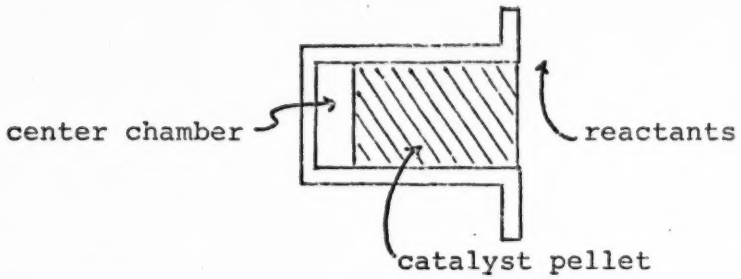
$K_{CO} = 3.15 \exp(2{,}900/RT)$, atm^{-1}

The above rate equation is of the same form as found by Ayen and Ng [Air Water Pollut. Int. J. 10, 1 (1966)], but the expressions for the constants are different. Confirmation runs showed that rate equation could be extrapolated for use with CO concentrations of at least 12,000 ppm. The presence of CO_2 in the reactant stream did not affect the rate of NO reduction. The activity of the copper chromite catalyst was found to increase in reducing atmospheres and decrease in oxidizing atmospheres.

The results of this investigation lead to several questions. Statistical mechanical formulation of the exponential expression for K_{CO} showed conclusively that the pre-exponential term cannot be greater than one. The model upon which the above rate equation is based does not provide for the formation of N_2O as an intermediate product. This species has been observed in the products of this reaction at 120-200°C [Otto and Shelef, J. Catal. 10, 408 (1968)]. These anomalies do not detract from the worth of the above empirical rate equation for design purposes but suggest that the model from which it is derived does not completely describe the actual reaction.

A further conclusion of Mr. Force's work was that the state of oxidation of the copper chromite catalyst affected its activity with regard to the CO-NO reaction. This effect has also been reported by Otto and Shelef [J. Catal. 10, 408 (1968)]. Although it was found that the catalyst activity increases in the reduced

state, there is still some controversy as to what oxidation state is more desireable and the rapidity with which changes in oxidation will occur as the gas stream changes its character from oxidizing to reducing. In an effort to examine these questions further, Mr. Hunter has undertaken a study of the NO-CO reaction in a single pellet reactor. In this type of reactor reactants are flowed past one end face of a cylindrical catalyst pellet while products and reactants are allowed to accumulate in a small dead space at the opposite end of the pellet (see diagram).



Under steady-state conditions the gas composition in the center chamber corresponds to that which would occur at the center plane of a catalyst pellet which is twice the length of the experimental one and exposed to reactants at both ends. Petersen and Balder [Chem. Eng. Sci. 23, 1287 (1968)] have shown that when such a reactor is operated under conditions of diffusion influence the gas composition at the center plane is very sensitive to small changes in catalyst activity and therefore can be used to monitor such changes.

Construction of a single pellet reactor and supporting equipment has been completed. The distinguishing features of this apparatus are the stainless steel bellows pump which was designed to recirculate the reacting gases at catalyst temperatures (250-500°C) and the use of a helium detector to detect the gas chromatography peaks. A limited number of runs were performed with the apparatus and confirmed that the reactor was indeed being operated in a diffusion limited regime. It was also confirmed that the oxidation state and catalytic activity of the catalyst may vary in the presence of an oxidizing or reducing atmosphere.

In a second new project Mr. J. London has begun an investigation of the mechanism of the NO-CO reaction. Of particular interest is the behavior of the reaction at low temperatures or high space velocities where the formation of N_2O rather than N_2 is preferred. Since the formation of N_2O is closely related to the manner in which the reactants are adsorbed on the catalyst surface and the types of reaction intermediates which are formed, it becomes necessary to examine the catalyst surface during the course of the reaction. The technique of infrared absorption

offers a relatively easy means for observing these species. For this purpose the catalyst (cuprous oxide) is supported on a very fine silica powder (Cab-O-Sil) which is then pressed into a thin disk. Since the Cab-O-Sil support is transparent to infrared radiation over a portion of the spectrum, it is possible to observe absorption bonds of molecules adsorbed on the catalyst. This technique has been used extensively for static adsorption studies [L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press (1966)] and in a few instances as a tool in support of kinetic studies.

To date Mr. London has completed construction of a reactor which also serves as an infrared absorption cell. The reactor has been incorporated into a recycle loop. High recirculation rates in the loop relative to the rates at which reactants are fed to and products removed from the loop allow the reactor to be operated in a differential manner at the same time that high overall conversions are obtained. Product compositions are to be determined by a gas chromatograph using a helium detector.

The equipment is currently being calibrated and experiments will be initiated shortly. Primary attention will be directed at taking kinetic data as well as infrared spectra with the objective of learning more about the mechanism of the NO-CO reaction.

Publications:

1. R. J. Ayen and A. Amirnazmi, Catalytic Reduction of Nitrogen Dioxide with Hydrogen, I&EC Process Design and Develop. 9, 247 (1970).

2. R. J. Ayen and J. W. Ault, Catalytic Reduction of Nitrogen Oxide with Various Hydrocarbons, A.I.Ch.E. J. 17, 265 (1971).

3. E. L. Force and R. J. Ayen, Catalytic Reduction of 50-5000 Parts-per-Million Nitric Oxide by Carbon Monoxide, presented at 69th National meeting of the AIChE, Cincinnati, Ohio, May 16-19, 1971, and to be published in a CEP Symposium Series.

Theses:

1. Rajinder K. Mahendroo, "Catalytic Reduction of Nitric Oxide with Ethane," June 1971.

2. Ali Amirnazmi, "Catalytic Reduction of Nitrogen Dioxide by Hydrogen," March 1968.

3. Joseph W. Ault, "Catalytic Reduction of Nitric Oxide with Various Hydrocarbons," September 1968.

4. Edwin L. Force, "Catalytic Reduction of 50-5000 Parts-per-Million Nitric Oxide by Carbon Monoxide," June 1969.

5. James C. Hunter, "The Development of a Single Pellet Reactor System for the Reaction of NO and CO over Copper Chromite," June 1971.

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